"Draft" Process Heater Work Group Response to Coordinating Committee Questions

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Note: The attached represents the Process Heater Work Group's response as of 9/4/97. As noted in the specific answers to Question 4 in particular, additional information will be developed to enhance the responses to Question 4 and the second part of Question 3, both of which are concerned with emissions of trace contaminants.

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On July 22, 1997, representatives of the Process Heater Work Group made a presentation to the Coordinating Committee. Copies of the EER review paper **"Organic Hazardous Air Pollutant Emissions from Gas-Fired Boilers and Process Heaters"** were distributed to the Coordinating Committee. The review paper contains most of the figures presented with additional explanations. The purpose of the presentation was to inform the Coordinating Committee of:

- Expected HAP emissions, and
- Preliminary MACT floor findings for indirect, gaseous fuel fired process heaters.

The presentation consisted of:

- Data from the Petroleum Environmental Research Forum study **"The Origin and Fate of Toxic Combustion Byproducts in Refinery Heaters and Boilers"** (Controlled experimental measurements of emissions from a full-scale commercial burner installed in a simulated furnace at the Sandia National Research Laboratory.)
- Energy and Environmental Research's evaluation of the Western States Petroleum Association/American Petroleum Institute Database of boiler and process heater air emissions. (Actual operating data from process heaters and boilers at several petroleum industry facilities.)
- A preliminary explanation of the in-place controls on indirect, gas-fired process heaters, and the impact of this analysis on the MACT floor for these sources.

Prior to the presentation, the Coordinating Committee facilitator informed the Committee that there was not a consensus on these issues within the Process Heater Work Group. Following the presentation, several questions were raised. The Coordinating Committee developed the following guidance for the Work Group to respond to by the next Coordinating Committee meeting:

1. Data

   - Make data open and publicly available.

   - Provide detail on test methods so their adequacy can be assessed.

2. How representative were the facilities tested? (e.g. West, Midwest, East)

3. Identify and explain why certain HAPs were and were not examined. Identify organic and inorganic HAPs as fuel constituents and HAP emissions. Are there HAP emission effects caused by process equipment and control devices, if present, on indirect-fired process heaters?

4. Identify the HAPs of interest resulting from input trace constituents such as chlorine and mercury.

An itemized response to the Coordinating Committee's request follows:

1. Data

- **Make data open and publicly available.**

- **Provide detail on test methods so their adequacy can be assessed**

A. PERF Data

Copies of the Final Report (including all Appendices) for inclusion in the ICCR Docket were mailed to Bill Maxwell of US EPA the week of August 11th. An executive summary report was provided to EPA electronically for posting to their ICCR bulletin board. Thorough documentation of procedures and results was considered an essential and important part of this program. The project had research objectives, and thus was under the full control of the project participants. The report had not been released to the public due to special circumstances of the Cooperative Research and Development Agreement (CRADA) mechanism, which was developed by DOE to facilitate collaborative efforts between industry and the US DOE national laboratories. The CRADA protects the information for a period of 5 years, after which it becomes public. Unanimous consent of all participants to an early release of the data was required under the terms of the CRADA. Early release of the data allows those entities who chose not to participate in the PERF project equal and free access to all the data and "sweat equity" the actual participants paid $7 million for. In some cases, and the PERF Project Participants unanimously agreed this was such a case, the Participants may feel early release is justified. However, the PERF Project Participants feel this should be handled on a project-by-project basis. Allowing free and equal access to all multi-million dollar cooperative research projects funded by the participants quickly

reduces the number of participants below the critical mass required to actually conduct projects. If the PERF Project Participants had been told up-front that all entities would have free and equal access to the project results whether or not they contributed funding, manpower, in-house data, etc., the PERF project may not have happened and the significant improvements in the technical understanding of combustion may not have occurred.

During the test planning stage of the project, it was recognized that it would be highly desirable if the results were acceptable to EPA; therefore, EPA's input to the test plan was sought and obtained before any tests were performed. To facilitate EPA's assistance in developing the plan, a detailed Quality Assurance Project Plan was prepared based on EPA Category II requirements (on scale of I to IV, with I being the highest) - suitable for rulemaking/policy decisions in conjunction with other results. The QAPP was reviewed by EPA Emission Measurement Center staff (Bill Grimley, et al.) and by EPA Office of Research and Development staff (Larry Johnson, et al. - test methods development, Andy Miller - combustion research). EPA staff provided many helpful comments, which were incorporated into the final plan. In addition to this external QA review by EPA, the QAPP was reviewed by all the project participants - including the scientific staff of the Sandia National Laboratories Combustion Research Facility (one member of which subsequently joined Stanford University as assistant professor), the chairman of the UCLA Chemical Engineering Department, and scientific and engineering staff of the industry participants. These are considered among the foremost experts in the world on combustion, with numerous publications in prestigious peer-reviewed journals on the topic. The final QAPP documents the test methods and quality assurance/quality control procedures used throughout the program. EPA commended the participants for the thoroughness of the plan, commenting that it was one of the best they had ever seen.

The test methods were based on EPA test methods. Four HAP test methods were used to characterize the organic compounds targeted in the PERF study:

- EPA Method 0040, an integrated bag sampling method with analysis by cryogenic preconcentration gas chromatography for light volatile organics;

- EPA Method 0031, using sample concentration on Tenax sorbent and analysis by purge-and-trap gas chromatography/ mass spectrometry for heavy volatile organics.

- EPA Method 0010, using sample concentration on XAD-2 sorbent and analysis by high-resolution gas chromatography/high resolution mass spectrometry for semivolatile organics (PAH). The quality control procedure was modified slightly to incorporate improvements reflected in California Air Resources Board Method 429.

- California ARB Method 430, with sample collection in impingers containing dinitrophenylhydrazine solution and subsequent analysis by high performance liquid chromatography with ultraviolet detection for aldehydes. The sampling and analysis

procedures are analogous to EPA Method 0011/0011A, except that midget impingers are used to reduce the potential for sample contamination (a chronic problem with the EPA method).

Another consideration was in providing a link between the test results and field test results; thus, it was desirable to use methods similar to those used to characterize actual field units so results would be comparable. All of these methods are considered by EPA to be the best methods currently available for providing unambiguous results from gas-fired external combustion sources.

Throughout the two-year testing phase of the program, EPA provided technical review support to the program. Andy Miller of the EPA Office of Research and Development provided valuable input during the many review meetings (about 3 per year) held during the program. Thus, in addition to internal review of the test results by all the leading scientists and engineers directly involved in the project, EPA was involved directly in evaluation of the test results in addition to development of the test plan. This is part of the basis for EPA's statement that they consider this to be an excellent program.

B. Field Data

These data reflect field tests on actual California petroleum industry process heaters and boilers performed to comply with a California law passed in 1988 known as AB2588. California Air Resources Board (CARB) was charged with enforcing the law, which required source testing under certain circumstances (refer to the law and related CARB guidance documents for details). CARB recognized that validated test methods for many pollutants did not exist for many of the sources to be tested; therefore, they embarked on a program to develop and/or validate many air toxics test methods so that the law would be enforceable. Many of these methods were still evolving and improved over the ensuing years as analytical techniques improved and/or field experience revealed quality control problems. As part of the law, those companies who were required to test also were required to submit test protocols before performing the tests, which were reviewed by CARB (or local agencies to which CARB delegated) for appropriate test methodology and approval before tests were performed. If a company failed to receive CARB approval prior to testing, they ran the risk of CARB rejecting the results (which CARB did in many cases where appropriate methodologies were not followed).

CARB also recognized that testing for all 300+ HAPs would be prohibitive and an excessive burden on industry. Roughly $20 million to $80 million or more has been spent by California industries in source tests alone (based on approximately 2000 test reports in CARB's inventory, at roughly $10,000 to $40,000 per test) to comply with this law. Under the law, CARB specified exactly which air toxics (a category of 300+ -- later 400+ -- substances which includes most of the HAPs which EPA listed in Title III of the 1990 Clean Air Act Amendments) should be measured for each specific source category. Since the law was directed at identifying health risk, it is likely that CARB's intent was to prioritize industry's resources by characterizing those air toxics

that CARB's engineering and scientific staff judged as being the most significant contributors to health risk from each source category. Thus, CARB, not the affected industries who paid for the tests, was in control of the scope of testing, testing methodology and acceptance of the results.

2. How representative were the facilities tested (e.g., West, Midwest, East)?

This problem could be addressed from two viewpoints:

- How do the test unit characteristics (design/duty, size, fuel, pollution controls, etc.) compare to the rest of the nation's inventory?

All of the field data were collected at California facilities. The simulated fuel gas mixtures used in the PERF study were formulated based on 19 actual fuel gas mixtures used at 5 petroleum facilities. All five of the facilities may not have been in California. The EPA ICCR database can possibly be used to compare population characteristics for different geographical areas. Since California has stringent NOx control regulations, it is likely that the California sources have a greater preponderance of NOx controls than do sources in the rest of the nation. While crude oils and their compositions vary by geographic region, the hydrocarbon constituents in fuel gases are uniform. The hydrogen content and the distribution of the hydrocarbons may vary somewhat between different fuel gases. The majority of fuel gas used in petroleum refineries will have approximately the same heating value as natural gas.

- How do the HAP emission test results compare to those from the rest of the nation's population?

Since very little high-quality HAP emission test data for gas-fired petroleum industry process heaters and boilers has been generated outside of California, this is difficult to assess directly. The STIRS database being developed under the ICCR process will help to facilitate this assessment. Emission factors developed for this project compare well to emission factors developed for natural gas fired external combustion sources reported by EPRI (part of the EPA's utility boiler HAPs docket for utility boilers), by CARB based on tests reported for natural gas fired utility boilers in the California Air Toxics Emission Factors (CATEF) database, and by EPA for natural gas fired external combustion sources in the most recent AP-42 emission factor draft update (April 1997). Thus, the combined results of all these studies begin to paint the same picture with respect to HAP emission factors. Also, it may be possible to obtain data from other testing done previously. New Jersey testing on gas-fired boilers, the Stanford report, and the 1990 HAPs report are possible sources of additional data for comparison.

3. Identify and explain why certain HAPs were and were not examined. Identify organic and inorganic HAPs as fuel constituents and HAP emissions. Are there HAP emission effects caused by process equipment and control devices, if present, on indirect-fired process heaters?

For the California field tests mandated under AB2588, the HAPs measured during tests were specified by CARB in the law and related guidance documents. To assure results would be accepted by CARB, the affected companies did not deviate from these specifications. As discussed above, the specific HAPs measured from each source category were likely selected to characterize those that were believed by CARB to pose the greatest health risk by that source category.

In the PERF project, the scientists and engineers involved in the project, who are internationally recognized experts in the combustion field, were faced with getting the most information possible out of a finite funding budget. Thus, target HAPs were selected to provide data that could be used to elucidate HAP formation/destruction/emission mechanisms, to provide a link between the research furnace and actual field units, and to characterize the HAPs believed to be of most significance on either a mass emission or health risk basis.

The fuels used in the PERF project were pipeline natural gas and pure hydrocarbon mixtures designed to simulate the range of natural gas and refinery gas compositions found in practice. Natural gas analyses have consistently shown chlorine levels to be below the detection limit of 0.2 ppmv. Pure commercial-grade hydrocarbons contain no chlorine. Actual petroleum refinery data submitted to CARB in response to AB2588 requirements shows total chlorine emissions of 0 lbs on both an annual and an hourly basis for process heaters and boilers. Thus, no attempt was made to characterize chlorinated organics such as 2,3,7,8-tetrachlorodibenzo-p-dioxin. Additionally, testing is currently underway to characterize dioxin and furan emissions from catalytic reforming units in petroleum refineries. This testing is being done under the Petroleum Refinery MACT II regulatory development activities covering vents from catalytic reforming units, catalytic cracking units, and sulfur recovery plants. Other than cooling towers which use chlorine as a disinfectant just like swimming pools and municipal water systems, the catalytic reformer unit's catalyst regeneration process is the only place chlorine is used in a petroleum refinery. There is no combustion associated with cooling towers. While crude oil can contain salt, the first process in the petroleum refinery is a desalting operation to remove all salt present. There is no combustion associated with the desalting process. Salts, particularly those with chloride ions, are severely corrosive to the carbon steel used in the majority of petroleum refinery vessels including process heaters and boilers. In addition to being severely corrosive, salts also form deposits in lines and vessels causing restrictions and blockages to fluid flow.

Approximately $7 million was spent on the PERF project. This effort resulted in the significant amounts of actual emissions testing described as well as significant improvements in computer models for formation and destruction of benzene, toluene, phenol, and naphthalene. The chemical reaction set for these constituents constitute more than 400 additional chemical reactions. Sandia's state-of-the-art computer workstations require about 24 hours to solve these reactions.

The only add-on controls currently in use on indirect, gas-fired process heaters are for NOx control. We are not aware of any impact of these controls on HAP emissions. In fact, both the PERF study and the WSPA/API study show no impacts of NOx controls on HAP emissions from

gas-fired process heaters or boilers. Potential sources of contaminants caused by process equipment or control devices could include refractory materials, intake fans, control devices using HAP-containing fluids, and the ambient air. The vast majority of indirect, gas-fired heaters are natural draft meaning they have no intake fans.

4. Identify the HAPs of interest resulting from input trace constituents such as chlorine and mercury.

After much discussion at our July meeting, the Process Heater Work Group decided that there are many ways and many issues to be addressed in order to properly answer this question. For example, there may be ways to answer this question as well as the second part of question 3 that are more cost-effective than conducting actual testing. The Process Heater Work Group formed a small subgroup to develop a plan for addressing this question. Since many of the same issues are applicable to gas-fired boilers, the Boiler Work Group was invited to add representative(s) to the small subgroup. Since this question appears applicable to all sources, the other source Work Group's may wish to add representative(s) also. The dioxin primer scheduled for the September ICCR meeting and any resulting Coordinating Committee guidance may have significant impact on how the small subgroup proceeds. Thus, while the small subgroup will begin discussions on how to proceed prior to the September ICCR meetings, no substantive decisions will be made prior to the September ICCR meetings.